

## DETERMINING SORPTION RATE BY A CONTINUOUS GRAVIMETRIC METHOD

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### ABSTRACT

A rate-determining step in the decontamination of chemical agent resistant coating (CARC) is thought to be the rate of solvent sorption into the pores of the paint. Because of systematic errors inherent in the conventional "blotting" method, a continuous gravimetric method was developed to determine the initial sorption rates of various solvents into MIL-C-53039A CARC and total amounts of solvent sorbed ( $t=30$  min). Using an HP Vector VL computer interfaced with a Mettler AX205 Delta Range balance, mass and time were automatically recorded in an Excel file while CARC coupons were submerged in solvent. Initial sorption rates were determined for butyl acetate, butyl ether, cyclohexane and propylene carbonate. A comparison between total sorption values ( $t = 30$  min) from the continuous gravimetric method and values from the "blotting" method (ASTM D543) shows a statistical difference between the two methods for CARC coupons.

### INTRODUCTION

The Applied Test Team and the Decontamination Team at the Edgewood Chemical-Biological Center (ECBC) are working to identify solvent properties that correlate with decontamination efficacy. It is believed that solvents that readily enter the pores of materials would be most effective in removing agent from porous surfaces. This particular study focuses on the sorption of various solvents into chemical agent resistant coating (CARC). Although Sidman, Schwoppe, Steber and Reid had previously studied sorption of organic liquids on polyurethane and alkyd-coated surfaces,<sup>1</sup> a study linking sorption of solvent into CARC with decontamination efficacy has not been done.

Traditionally, sorption studies are performed using the guidelines described in ASTM D543,<sup>2</sup> which call for repeatedly removing a specimen from solvent, blotting with tissue and weighing. When using this method to determine initial sorption rates (diffusion coefficients), the associated random error for elastomers exposed to solvents having a boiling point of 121°C or less ranges from  $\pm 7$ -17%.<sup>3</sup> To effectively measure initial sorption rates of volatile solvents, a continuous gravimetric method was developed. This alternative method allows mass readings to be automatically recorded to file while the specimen is submerged in solvent and therefore reduces the number of times the material needs to be physically handled. Because the sample does not need to be removed and blotted, mass readings can be recorded more frequently.

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## OBJECTIVE

The objectives of this study were to determine initial sorption rates and total amounts of solvent sorbed ( $t = 30$  min) by CARC exposed to selected solvents, compare total sorption values with those obtained by ASTM D543 values, and determine whether a linear correlation exists between sorption rate and solvent properties such as viscosity, surface tension, molecular volume, and Hildebrand solubility and capillary transport scaling parameters.

## EXPERIMENTAL

### Materials and Chemicals

Butyl acetate, butyl ether, cyclohexane and propylene carbonate were obtained from Aldrich Chemical Company, Milwaukee, WI. CARC (Hentzen, High PVC, Mil-C-53039, HAPS-free, Green 383, RLE/6/131/RS%-146) was obtained from the Army Research Laboratory (ARL) at Aberdeen Proving Ground. Wire mesh (0.003" diameter and 0.011" x 0.011" cell size) was obtained from Sefar America Inc., Briarcliff Manor, NY.

### Procedure

#### *Specimen Preparation*

CARC coupons were prepared by dipping wire mesh rectangles into CARC paint. The freshly dipped CARC strips were allowed to dry over a period of three days in a ventilation hood under normal laboratory conditions ( $\approx 70\%$  RH and  $25\text{ }^{\circ}\text{C}$ ). Each CARC coupon was approximately 40 mm X 25 mm X 0.20 mm and weighed less than one gram. A hole (1/16" diameter) was drilled near the top of each coupon for placement on the weighing hook. Prior to use, each specimen was washed with an oil-free soap, blotted with a lint-free tissue and allowed to dry at room temperature for at least 24 hours. Dimensions and mass of each specimen were measured. Mild steel non-painted coupons (40 mm X 25 mm X 0.05 mm) were used as negative controls.

#### *Continuous Gravimetric Method*

A Mettler Toledo AX205 Delta Range® balance was placed on a support above the laboratory bench and enclosed in a custom-made plastic case with door. The balance was configured for beneath the balance weighing by attaching wire and hook to the weighing pan. A double wall glass vessel was secured on a laboratory jack beneath the balance. The vessel was filled with solvent and covered. The temperature of the solvent was maintained at  $22\text{--}25\text{ }^{\circ}\text{C}$  by a Haake A-80 bath circulator connected to the vessel. A hose connected to a vacuum pump and carbon filter was placed through an opening in the cabinet for ventilation of solvent vapors. A Hewlett Packard Vectra VL computer equipped with a Pentium III processor, Windows 2000 and Microsoft Excel was linked to the balance with Mettler Balance Link Software to automatically record data. A coupon was suspended beneath the balance and the transfer of mass readings to an Excel spreadsheet was initiated immediately. After the first stable reading, the vessel was uncovered and the lab jack was raised until the coupon was completely submerged in solvent. Mass readings were automatically recorded every 20 s for 0.5 h. At the end of this period, the CARC strip was removed from solvent and the data file was saved. A minimum of three coupons was tested for each solvent.

#### *ASTM D543*

A specimen was completely submerged in solvent for 0.5 h. Afterwards, all visible excess liquid was blotted away using a lint-free tissue. The blotted specimen was then weighed and its post-exposure dimensions were measured. At least three coupons were tested for each solvent.

#### *Calculations*

**Weight gain** (g) was calculated by subtracting initial mass from final mass (eq 1). For the continuous gravimetric method, initial mass was the first mass recorded once the specimen was completely submerged in solvent and final mass was the last mass recorded before the specimen was removed.

$$\text{Weight gain (g)} = \text{final mass (g)} - \text{initial mass (g)} \quad (1)$$

Weight gain was used to calculate **total amount of solvent sorbed per surface area** ( $\mu\text{g}/\text{cm}^2$ ) for each specimen (eq 2). The surface area of each specimen was calculated based on pre-exposure dimension measurements.

$$\text{Mass sorbed per area } (\mu\text{g}/\text{cm}^2) = [\text{weight gain (g)}/\text{surface area (cm}^2)] \times [1 \times 10^6 \mu\text{g}/\text{g}] \quad (2)$$

**Change in volume** of the specimen (eq 3) was calculated based on pre-exposure and post-exposure dimension measurements.

$$\text{Change in volume (cm}^3) = \text{final volume (cm}^3) - \text{initial volume (cm}^3) \quad (3)$$

Equation 4, which illustrates Archimedes' buoyancy principle, was used to predict **apparent mass** or the mass of the specimen while submerged in solvent:

$$\text{Apparent mass (g)} = \text{mass in air (g)} - [(\text{mass in air (g)}/\text{density of object (g/cm}^3) \bullet \text{density of solvent (g/cm}^3)] \quad (4)$$

Equation 5, which was derived from eq. 4, shows the theoretical relationship between mass gains observed with the continuous gravimetric method and mass gains observed with ASTM D543 and can be used to predict how swelling of the specimen will affect the observed continuous gravimetric gains. "Δ mass" (referred to below) is obtained by ATSM D543.

$$\frac{\text{Cont. Grav. Gain (g)}}{\text{ASTM 543 Gain (g)}} = 1 - [\Delta \text{ volume (cm}^3)/\Delta \text{ mass (g)} \bullet \text{density of solvent (g/cm}^3)] \quad (5)$$

**Propagation of error** was computed for calculated volumes by using Equation 6 shown below<sup>4</sup>, where "s" represents standard deviation, "y" represents the calculated volume, and "x," "w," and "z" each represent average length, width and thickness measurements.

$$s_y = y [(s_x^2/x^2) + (s_z^2/z^2) + s_w^2/w^2]^{1/2} \quad (6)$$

**Initial Sorption Rates** ( $\mu\text{g}/\text{cm}^2/\text{h}^{1/2}$ ) were determined by calculating the slope of the linear portion of mass sorbed per area versus square root of time plots (Fick's Law Plots).

**Hildebrand solubility parameter** ( $\delta$ ) was calculated for some solvents using eq. 7, where  $\Delta H_v$  is heat of vaporization (cal/mol) and  $V_m$  is the molecular volume ( $\text{cm}^3/\text{mol}$ ).

$$\delta = (\Delta H_v - RT)/V_m^{1/2} \quad (7)$$

The **capillary transport scaling parameter**<sup>5</sup> was calculated using eq. 8.

$$\text{Capillary transport scaling parameter} = \left[ \frac{\text{Surface tension (dyn/cm)}}{\text{Viscosity (mPa at 25}^\circ\text{C)}} \right]^{1/2} \quad (8)$$

## RESULTS

### Initial Sorption Rates

After approximately two minutes ( $t^{1/2} = 0.2 \text{ h}^{1/2}$ ), CARC began to sorb solvents at a slower rate than observed initially (Figure 1). Therefore, the first two minutes of sorption were used to determine the initial sorption rates (Table 1).

Figure 1. Fick's Law Plot for CARC coupons exposed to various solvents at 25°C for 30 min.

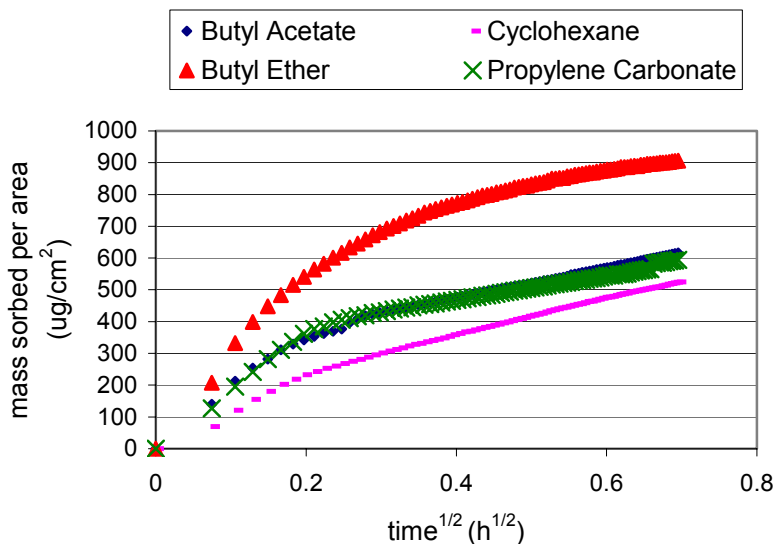


Table 1. Initial sorption rates with corresponding standard deviation and  $R^2$  values for CARC coupons exposed to various solvents at 25°C for 2 min.

Solvent	Average Initial Sorption Rate ( $\mu\text{g}/\text{cm}^2/\text{h}^{1/2}$ )	Standard Deviation (%)	$R^2$
Butyl ether	2840	23.2	0.983
Butyl acetate	1810	43.1	0.980
Propylene Carbonate	1840	46.0	0.997
Cyclohexane	1180	36.6	0.992

CARC coupons sorbed butyl ether at a faster rate ( $2840 \mu\text{g}/\text{cm}^2/\text{h}^{1/2}$ ) than any of the other solvents. Initial sorption rates for propylene carbonate and butyl acetate were similar, each having an average rate of approximately  $1800 \mu\text{g}/\text{cm}^2/\text{h}^{1/2}$ . Cyclohexane was sorbed at the slowest rate ( $1180 \mu\text{g}/\text{cm}^2/\text{h}^{1/2}$ ). Analysis of variance (ANOVA)<sup>6</sup> shows that initial sorption rates among propylene carbonate, cyclohexane, and butyl acetate were statistically similar (P-value = 0.52). The sorption rate of butyl ether was significantly different (ANOVA, P-value = 0.15) from the rates of the other solvents. Percent standard deviations for cyclohexane and butyl acetate results were about 40%, and deviation for propylene carbonate was 50%. Butyl ether results had the least amount of deviation ( $\approx 20\%$ ).

### Total Sorption Values

A comparison of the total sorption data obtained by the continuous gravimetric and ASTM D543 methods is provided in Table 2. Steel coupons (controls) sorbed less than  $20 \mu\text{g}/\text{cm}^2$  of butyl ether, butyl acetate and cyclohexane by both methods. Steel exposed to butyl acetate had a negative total sorption value by the continuous gravimetric method, suggesting a possible loss of mass. There was no statistical difference between total sorption values of steel controls obtained by the continuous gravimetric method and those obtained by the ASTM D543 (student t-test, 95% C.I., P-value = 0.67) <sup>6</sup>. Standard deviation of ASTM D543 steel total sorption values was larger than deviation of continuous gravimetric method values for steel exposed to butyl ether and cyclohexane.

Table 2. Average amount of solvent sorbed ( $\mu\text{g}/\text{cm}^2$ ) with 95% confidence interval by steel controls and CARC Specimens at 25 °C in 30 min.

Solvent	Sample	<sup>a</sup> Method I	<sup>a</sup> Method II
Butyl acetate	Controls	$-7.47 \pm 5.20$	0
	CARC	$622 \pm 265$	$1427 \pm 415$
Butyl Ether	Controls	0	$3.37 \pm 21.2$
	CARC	$918 \pm 496$	$1190 \pm 376$
Cyclohexane	Controls	$13.4 \pm 6.32$	$12.6 \pm 39.7$
	CARC	$533 \pm 190$	$837 \pm 234$
Propylene Carbonate	Controls	-----	-----
	CARC	$595 \pm 597$	$899 \pm 225$

<sup>a</sup>Method I refers to continuous gravimetric data <sup>b</sup>Method II refers to ASTM D543 values.

Continuous gravimetric total sorption values for CARC were roughly 60% of ASTM D543 CARC values (Table 3). CARC total sorption values obtained by the continuous gravimetric method averaged  $700 \mu\text{g}/\text{cm}^2$ , whereas values obtained by ASTM D543 averaged  $1100 \mu\text{g}/\text{cm}^2$  (Table 2). CARC coupons sorbed more butyl acetate and butyl ether than propylene carbonate and cyclohexane in both methods. However, more butyl acetate ( $1427 \mu\text{g}/\text{cm}^2$ ) than butyl ether ( $1190 \mu\text{g}/\text{cm}^2$ ) was sorbed in ASTM D543. Continuous gravimetric method sorption values were statistically different from ASTM D543 values for CARC exposed to butyl acetate, butyl ether, and cyclohexane (Student t-test, 95% C.I.,  $0.0048 \leq \text{P-value} \leq 0.032$ ) <sup>6</sup>. There was no significant difference between the methods when comparing sorption values for CARC exposed to propylene carbonate ( $P = 0.102$ ).

Table 3. Ratio of continuous gravimetric to ASTM D543 total sorption values (t= 30 min)

Solvent	Cont. Grav. /ASTM D543
Butyl Ether	0.771
Butyl Acetate	0.436
Cyclohexane	0.637
Propylene Carbonate	0.662

### Change in Volume

The average change in volume for specimens exposed to butyl acetate, butyl ether, cyclohexane and propylene carbonate is listed in Table 4. CARC exposed to butyl ether, propylene carbonate and cyclohexane experienced a decrease in overall volume. Steel exposed to cyclohexane also showed a volume decrease. The largest calculated decreases were for steel exposed to propylene carbonate (-12%)

and CARC exposed to butyl ether (-10%). CARC exposed to butyl acetate and steel exposed to butyl ether experienced a 1 – 3% increase in volume.

Table 4. Average percent change in volume of steel controls and CARC specimens exposed to various solvents at 25°C for 0.5 h.

Solvent	Sample	$\Delta$ Volume (%)
Butyl acetate	Controls	----
	CARC	1.3
Butyl Ether	Controls	2.3
	CARC	-10.0
Cyclohexane	Controls	-3.8
	CARC	-7.6
Propylene Carbonate	Controls	-12.0
	CARC	-0.9

#### *Sorption Rate versus Solvent Properties*

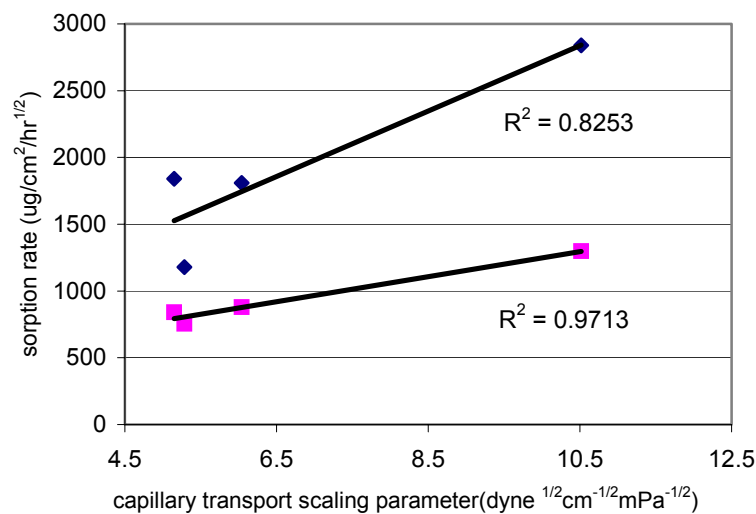
CARC sorption rates over two minutes and 30 minutes were compared to the molecular volume, viscosity, surface tension, Hildebrand solubility parameter ( $\delta$ ), and capillary transport scaling parameter of the studied solvents (Table 5). Sorption rates over 30 minutes were calculated by dividing the continuous gravimetric total sorption value ( $t = 30$  min) by the square root of exposure time. Less viscous solvents (butyl ether and butyl acetate) seemed more readily sorbed by CARC than more viscous solvents (cyclohexane and propylene carbonate). However, propylene carbonate's viscosity is more than twice the viscosity of cyclohexane but was sorbed more quickly than cyclohexane. With the exception of propylene carbonate, solvents having a high molecular volume and low  $\delta$  were sorbed more quickly than solvents with lower molecular volumes and higher  $\delta$ . Although propylene carbonate has the lowest molecular volume and the highest value for its Hildebrand solubility parameter, it had the second highest sorption rate over two minutes. Solvents with higher surface tensions were sorbed more rapidly in two minutes than solvents with lower surface tensions. There was a significant linear correlation ( $R^2 = 0.971$ ) between sorption rates over 30 minutes and the capillary transport scaling parameter (Figure 2). This correlation was not as strong when comparing the two-minute rates ( $R^2 = 0.825$ ).

Table 5. Sorption rates over two minutes and 30 minutes for CARC versus molecular volume, viscosity, surface tension, Hildebrand solubility parameter and capillary transport scaling parameter.

Solvent	Sorption Rates ( $\mu\text{g}/\text{cm}^2/\text{h}^{1/2}$ )	Molecular Volume ( $\text{cm}^3/\text{mol}$ )	Viscosity <sup>7</sup> (mPa at 25 °C)	Surface Tension <sup>8</sup> (dyn/cm at 20 °C)	Hildebrand Solubility Parameter <sup>c</sup> ( $\delta$ )	Capillary Transport Scaling Parameter (dyne <sup>1/2</sup> /cm <sup>1/2</sup> • mPa <sup>1/2</sup> )
Butyl Ether	<sup>a</sup> 2840 <sup>b</sup> 1300	170.46	0.637	70.44	<sup>c</sup> 6.9	10.5
Butyl Acetate	1810 880	131.70	0.685	25.0	<sup>c</sup> 7.8	6.04
Propylene Carbonate	1840 841	84.67	2.53	67.11	<sup>d</sup> 13.3	5.15
Cyclohexane	1180 754	108.04	0.894	24.98	<sup>d</sup> 8.2	5.29

<sup>a</sup>2 min <sup>b</sup>30 min <sup>c</sup>Calculated using eq. 7.  $\Delta H_v$  obtained from reference<sup>7</sup> <sup>d</sup>Obtained from reference<sup>9</sup>

Figure 2. Sorption rates of various solvents into CARC over 2 minutes (◆) and 30 minutes (■) versus capillary transport scaling parameter.



## DISCUSSION

A possible explanation for the lower CARC total sorption values with the continuous gravimetric method may be swelling of the samples. According to eq. 5, a mass increase of the submerged specimen without a change in volume of the specimen would yield a weight gain identical to the value observed with ASTM D543. On the other hand, if the object were to swell, its density may decrease—causing the buoyancy effect on the object to increase and reducing the observable mass increase. Although change in volume calculations for the CARC specimens did not indicate swelling in most cases (Table 2), swelling may have still occurred. Results of propagation of error calculations (eq. 6) show that pre and post-exposure dimension measurements may not have been precise enough to detect small changes in volume. Most pre-exposure and post-exposure calculated volumes have a standard deviation of approximately  $\pm 0.02 \text{ cm}^3$  or  $\pm 10 \%$ . Change in volume, which results from the difference between pre- and post-exposure measurements, has a standard deviation of  $\pm 0.028 \text{ cm}^3$  or  $\pm 14\%$ . The volume changes listed in Table 2 range from  $-12$  to  $2\%$ . Possibly, the calculated changes in volume can be attributed to random error rather than an actual change in the volume of the specimens.

## CONCLUSION

Initial sorption rates were successfully determined for four solvents with the continuous gravimetric method. Total sorption values obtained by the continuous gravimetric method were statistically different from ASTM D543 values for three solvents, but comparable for propylene carbonate. A significant relationship between sorption rate and the capillary transport scaling parameter was identified. More data are required to identify potential relationships between sorption rate and other solvent properties. Identification of standard or control materials with well-characterized total pore volume would allow absolute calibration of the developmental method. A correction for swelling may enable use of the continuous gravimetric method as an alternative to ASTM D543. Pore characterization of CARC coupons may provide information on sorption processes as well as the accuracy of ASTM D543 and continuous gravimetric methods.



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